

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE
in its capacity as elected Office

Date of mailing (day/month/year) 19 March 2001 (19.03.01)	
International application No. PCT/KR99/00285	Applicant's or agent's file reference
International filing date (day/month/year) 10 June 1999 (10.06.99)	Priority date (day/month/year)
Applicant PARK, In, Hwan et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
10 January 2001 (10.01.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Olivia TEFY

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To:

HUH, Sang, Hoon
Hyecheon Building
13th floor
831, Yeoksam-dong
Kangnam-ku
Seoul 135-792
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 16 July 1999 (16.07.99)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference	International application No. PCT/KR99/00285

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY (for all designated States
except US)

PARK, In, Hwan et al (for US)

International filing date : 10 June 1999 (10.06.99)

Priority date(s) claimed :

Date of receipt of the record copy
by the International Bureau : 28 June 1999 (28.06.99)

List of designated Offices :

National :JP,US


ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
☒ confirmation of precautionary designations
☐ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: R. Chrem 
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Record Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is **20 MONTHS** from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, **30 MONTHS** from the priority date, provided that the election is made before the expiration of 19 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.

GR and ES became bound by PCT Chapter II on 7 September 1996 and 6 September 1997, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1996 and 6 September 1997, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit is the filing date of the earliest application whose priority is claimed.

PCT

**NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES**

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

T :
HUH, Sang, Hoon
Hyecheon Building
13th floor
831, Yeoksam-dong
Kangnam-ku
Seoul 135-792
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 21 December 2000 (21.12.00)		IMPORTANT NOTICE
Applicant's or agent's file reference		
International application No. PCT/KR99/00285	International filing date (day/month/year) 10 June 1999 (10.06.99)	Priority date (day/month/year)
Applicant KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

JP

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 21 December 2000 (21.12.00) under No. WO 00/77108

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

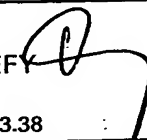
To:

HUH, Sang, Hoon
Hyecheon Building
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RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 19 March 2001 (19.03.01)		IMPORTANT INFORMATION	
Applicant's or agent's file reference			
International application No. PCT/KR99/00285 (161)	International filing date (day/month/year) 10 June 1999 (10.06.99)	Priority date (day/month/year)	
Applicant KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY et al			

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:
National :JP,US
2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:
None
3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer: Olivia TEFY  Telephone No. (41-22) 338.83.38
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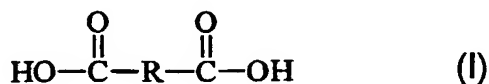
Published:

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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.



(54) Title: ANAEROBIC ADHESIVE COMPOSITION



(57) Abstract: The present invention relates to an anaerobic adhesive composition and more particularly, to the anaerobic adhesive composition which blends a difunctional carboxylic acid, expressed by formula (I), to the anaerobic adhesive

composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents, showing some useful physical properties; a) the rapid velocity in a hardening reaction, b) the good stability in long-term storage, and c) the break-loose torque which is sufficiently applied in the assembly of bolt-nuts, precision apparatuses and electric/electronic parts, wherein R is (CH₂)_n or CH₂C(=CH₂) and n is an integer in the range of 2 to 10.

WO 00/77108 A1

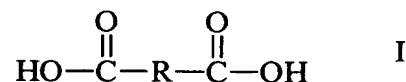
ANAEROBIC ADHESIVE COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to an anaerobic adhesive composition and more particularly, to the anaerobic adhesive composition which blends a difunctional carboxylic acid, expressed by the following formula I, to the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents, showing some useful characteristics;

10 a)the rapid velocity in a hardening reaction, b)the good stability in long-term storage, and c)the break-loose torque which is sufficiently applied in the assembly of bolt-nuts, precision apparatuses or electric/electronic parts:



15 wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(=\text{CH}_2)$ and n is an integer in the range of 2 to 10.

Description of the Related Art

For the enhancement of hardening velocity within the scope of an anaerobic adhesive composition not to have a poor effect on the stability during

20 long-term storage, the anaerobic adhesive composition of common type was prepared by chemicals such as monomers, oligomers, inhibitors, peroxide-typed oxidizers(e.g., hydrogen peroxide and cumene hydroperoxide) and reducers(e.g., amines and imides) as disclosed in the following conventional methods[European Patent Appln. No. 446,144(1991), 443,916(1991);

25 499,483(1992); and Japanese Patent Kokai No. Pyeong2-187,401]. Also, an oxidizer and a reducer were used together in the preparation of anaerobic adhesive composition, as described in the following methods: Hung. Telies Hu 44, 280(1988) as a method using a complex alkaline solution, US Patent No.

4,731,146 as a method using a copper compound, and closed German Patent No. 3,611,307 as a method using a phosphate compound, etc.

In order to improve the stability in storage, the anaerobic adhesive composition in its initial development stage was prepared in such a method
5 that an inhibitor was added to a mixture of monomers and oligomers: the oligomers are derived from multi-functional (metha)acrylates (Japanese Patent Kokai No. Sho43-6545, Sho44-852). Then, the inhibitor was used as a scavenger for radicals which can spontaneously generate in the state of preparation or storage.

10 Japanese Patent Kokai No. Sho46-3160, Sho57-83572 and Pyeong6-66308 disclosed the anaerobic adhesive composition containing acrylic acid, methacrylic acid or thiosalicylic acid in order to increase its break-loose torque.

Japanese Patent Kokai No. Sho52-39694 and Sho57-83572 reported that organic phosphates were added to the anaerobic adhesive composition so as to
15 improve both its break-loose torque and the stability in storage.

Closed German Patent No. 3,611,307 also reported that methylenediphosphonic acid was added to the anaerobic adhesive composition in order to increase its break-loose torque.

To improve the stability in storage, glycerol dimethacrylate esterified
20 by succinic acid anhydride was used as a component of the anaerobic adhesive composition, as described by closed German Patent No. 3,527,717.

In addition, in order to increase its break-loose torque, Japanese Patent Kokai No. Sho62-184,076 disclosed that methylsulfamic acid was added to the anaerobic adhesive composition, but it brought about corrosion on the surface
25 of metallic materials.

Further, when an anaerobic adhesive composition is used to assemble parts into a complete whole, the enhancement of adhesive force as well as workability is powerfully required toward higher productivity. In the anaerobic

adhesive composition, a reducer containing the groups like imides, mercaptos or amines is concurrently used with a peroxide-typed initiator, where it is very important to select a useful reducer/oxidizer catalyst.

As above-mentioned, in the case that an oxidizer and a reducer existing
5 in the same vessel, the anaerobic adhesive composition is very unstable under its coexistence and can be easily initiated by radicals spontaneously produced between them. Although it is extremely difficult that a hardening reaction in progress is stopped or controlled the reaction in storage at room temperature was generally controlled by the addition of inhibitor above-mentioned.
10 Therefore, it is previously added to a mixture of monomers and oligomers in the preparation of anaerobic adhesive composition.

For more application, the anaerobic adhesive composition always requires access to the proper regulation of physical properties like strength and flexibility by way of the enhancement of both the rapid velocity in hardening
15 and the stability in storage.

SUMMARY OF THE INVENTION

To be free from the above-mentioned shortcomings, a difunctional carboxylic acid is essentially added to an anaerobic adhesive composition in
20 this invention.

An object of this invention is to provide the anaerobic adhesive composition with the stability in storage as well as the rapid hardening in fastening by mixing the difunctional carboxylic acid, where the anaerobic adhesive composition as a product shows useful break-loose torque.

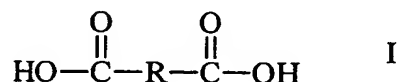
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Detailed Description of the Invention

This invention relates to an anaerobic adhesive composition which blends 0.0001 - 10 parts in weight of a difunctional carboxylic acid, expressed by

the following formula I, in proportion to 100 parts in weight of a mixture of monomers and oligomers, to the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents:

5



wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(=\text{CH}_2)$, and n is an integer in the range of 2 to 10.

This invention explains in more detail as follows:

10 The anaerobic adhesive composition applicable to prevent a bolt which is jointed nuts from releasing requires the rapid hardening in fastening as well as the stability in storage, thereby enhancing its break-loose torque and workability.

In this invention, the difunctional carboxylic acid expressed by formula I is largely mixed to a mixture of monomers and oligomers.

15 In Table 1 in this invention, the values of pK_a (acid dissociation constant) of aliphatic difunctional carboxylic acids gradually increased with increasing the values of n above-mentioned, and then slightly decreased with increasing the values of n above 2. Then, the values of pK_1 in non-aliphatic difunctional carboxylic acids were less than those of aliphatic difunctional carboxylic acids.
20 Especially, when the value of n was at zero, pK_1 was the lowest value in various difunctional carboxylic acids.

In relation to this, the anaerobic adhesive composition containing a difunctional carboxylic acid brings about a rapid hardening reaction as well as the stability in storage: as the value of n gradually increases, the acidity of
25 difunctional carboxylic acid decreases. The break-loose torque of the anaerobic adhesive composition also increases with shortening the hardening time, and then its molecular weight grows bigger.

From the observation for above tendency, the value of n is limited as an

integer in the range of 2-10 according to this invention, and then the difunctional carboxylic acid is in the range of 1-5 of pKa. Under such condition, since the carboxylic acid scarcely give any effects on the acidity of an oxidizer like cumene hydroperoxide, the stability in storage of the anaerobic adhesive composition gets better. The anaerobic adhesive composition showed useful break-loose torque caused by a rapid hardening reaction in the presence of difunctional carboxylic acid. When a bolt and a nut are jointed, the small quantity of air solubilized in the anaerobic adhesive composition is excluded, and at the same time a hardening reaction is initiated. The reaction proceeds of itself under the condition.

In the preparation of anaerobic adhesive composition of this invention, first of all, monomers, oligomers and inhibitors are mixed and agitated under oxygen atmosphere. Subsequently, each of reducers and oxidizers is added to the mixture, followed by the addition of difunctional carboxylic acid. Thereafter, in order to increase the viscosity of the anaerobic adhesive composition, polyethylene resin (particle size: below 10 μm) and fumed silica (particle size: below 5 μm) as thickening agents are added.

Monomers used in this invention are one or more selected from ethyleneglycol di(metha)acrylate, diethyleneglycol di(metha)acrylate, triethyleneglycol di(metha)acrylate, tetraethyleneglycol di(metha)acrylate, trimethylolpropane tri(metha)acrylate, styrene, chlorostyrene, vinyltoluene, α -methylstyrene, vinylacetate, methylacrylate, ethylacrylate, butylacrylate and methylmethacrylate.

Besides above monomers, oligomers used in this invention are one or more selected from mono or poly(metha)acrylate oligomer of bisphenolic compound, α, ω -diacryloyl-(bisethyleneglycol)-phthalate and α, ω -tetraacryloyl-(bistrimethylolpropane)-tetrahydrophthalate, and the acrylic oligomers containing aliphatic and aromatic urethane groups or polyether groups.

In order to get the enhancement of adhesive force through a rapid hardening reaction, a difunctional carboxylic acid, represented by formula I is used in this invention. The difunctional carboxylic acid is one or more selected from malonic acid, succinic acid, adipic acid, itaconic acid, pimelic acid, terephthalic acid and decanoic acid.

The quantity of difunctional carboxylic acid can be blended within 0.0001-10 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the amount is less than 0.0001 part in weight, the promotion of a hardening reaction may be negligible, but may be possible in the quantity more than 10 parts in weight: the storage stability of the anaerobic adhesive composition may be lowered, so that the composition of the carboxylic acid should be properly controlled within above range.

According to this invention, an inhibitor is one or more selected from hydroquinone, methylhydroquinone, hydroquinone monomethylether, naphthoquinone, penanthraquinone, anthraquinone, sebenzoquinone, catechol, *t*-butylcatechol, 2,6-*t*-butyl-4-methylphenol, phenothiazine, picric acid phenothiazine and hydroxydiphenylamine. In addition, a metal ion chelating agent is used one or more selected from ethylenediamine tetraacetic acid and its salt.

The quantity of inhibitor can be added 0.0001-3 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the quantity is less than 0.0001 part in weight, the effect of inhibition may be insufficient, finally lowering the stability in storage, but in the quantity more than 3 parts in weight, the break-loose torque may be lowered, as the hardening time lengthened.

According to this invention, the combination of oxidizer/reducer as an initiator is used. An oxidizer is one or more selected from *t*-butylhydroperoxide, cumenhydroperoxide, di-*t*-butylhydroperoxide, methylethylketoneperoxide,

dicumylperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, diisopropylbenzene hydroperoxide, *t*-butylbenzoate and *t*-butylperoxyacetate.

A reducer is one or more selected from phenyl- α -naphthylamine, *N,N'*-dimethyl-*p*-toluidine, *N,N'*-dimethylaniline, triethylenetetramine, 5 diethylenetriamine, tri-*N*-butylamine, *o*-benzoic sulfimide, acetylthiourea, ethylene thiourea and 2-mercaptobenzothiazole.

An initiator is used as the form combined one or more. The quantity of initiator can be added 0.001-10 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the quantity is less than 10 0.001 part in weight, the effect of initiation is insufficient, but in the quantity more than 10 parts in weight, the storage stability of the anaerobic adhesive composition may be lowered, so that the composition of the initiator should be properly controlled within above range.

Further features and advantages will be apparent from the following 15 examples containing some Tables. The following examples illustrate the ways in which the principle of this invention has been applied, but are not to be construed as limiting its scope.

20

25

Table 1. Anaerobic adhesive compositions blended difunctional carboxylic acids.

Run	Difunctional carboxylic acid				Anaerobic adhesive composition		
	Name	Structural formula	Acid dissociation constant*		Hardening time (min)	Break-loose torque (kg-cm)	Stability in storage**
			pK ₁	pK ₂			
1	Oxalic Acid	HO ₂ CO ₂ H	1.27	4.27	15	51	O
2	Malonic Acid	HO ₂ CCH ₂ CO ₂ H	2.83	5.70	13	73	O
3	Succinic Acid	HO ₂ C(CH ₂) ₂ CO ₂ H	4.21	5.64	10	57	O
4	Maleic Acid	HO ₂ C(CH=CH)CO ₂ H	1.91	6.33	10	85	O
5	Adipic Acid	HO ₂ C(CH ₂) ₄ CO ₂ H	4.42	5.41	8	93	O
6	Itaconic Acid	HO ₂ CCH ₂ C(=CH ₂)CO ₂ H	-	-	8	91	O
7	Pimellic Acid	HO ₂ C(CH ₂) ₅ CO ₂ H	4.50	5.40	10	49	O
8	Terephthalic Acid	HO ₂ C(C ₆ H ₄)CO ₂ H	2.95	5.40	14	69	O
9	Decanoic Acid	HO ₂ C(CH ₂) ₈ CO ₂ H	4.59	5.59	15	61	O
10	Cumene Hydroperoxide	C ₆ H ₅ C(CH ₃) ₂ OOH	12.60	-	-	-	O
11	None	-	-	-	30	30	O

* John A. Dean, Handbook of Organic Chemistry, Section 8, McGRAW-HILL, New York,

5 1987; Section 8, pp.8-2~8-55.

** The observation whether the viscosity increases or not; not noticed: O, noticed: X.

Examples ①~1-13:

By separate experiments as shown in Table 1 above-mentioned, anaerobic adhesive compositions containing difunctional carboxylic acids were prepared and briefly estimated: it was found that the anaerobic adhesive composition without a difunctional carboxylic acid exhibited longer hardening time and less break-loose torque, whereas the anaerobic adhesive composition

10

with it exhibited a hardening time less than 15 min. and the break-loose torque after 24 hr was also very useful.

In relation to this, the anaerobic adhesive composition (Table 2a, run ①~12) was prepared as follows. That is, 10g of ethyleneglycol dimethacrylate, 10g of 2-hydroxyethyl methacrylate and 10g of tetraethyleneglycol dimethacrylate as components of monomers and oligomers were added to a reactor with reflux condenser and agitated at 120rpm under 120cc/min of oxygen flow. Then, 0.05g of hydroquinone methylether as an inhibitor was added and agitated for 10mins, followed by the addition of 3g of cumene hydroperoxide as an oxidizer.

Thereafter, 0.15g of *o*-benzoic sufimide and 0.40g of *N,N'*-dimethyl-*p*-toluidine as reducers were added and then sufficiently agitated. Finally, 1.46g(0.010 mol) of adipic acid (cf. run 5 of Table 1) and 3.30g of polyethylene powder(5 μ m) were added and further agitated for 20min, consequently preparing an anaerobic adhesive composition of this invention.

In addition, some physical properties of the anaerobic adhesive composition were measured as follows:

- (1) Hardening time(min): after a part of bolt(1/4 inch of diameter, 3 inch of length) made by stainless steel is coated, a nut made by stainless steel as a counter part is loosely jointed on its coated surface at 25°C. A hardening time based on the earliest time until the nut is not moved by fingers is measured.
- (2) Break-loose torque(kg-cm): the bolt-nut was fastened at 25°C, and left to postcure at 25°C for 24 hrs. The test was performed by using a torque wrench.
- (3) Stability in storage: the anaerobic adhesive composition which a hardening reaction in a bath at 80°C didn't happen in 10 days was required.
- (4) Viscosity: the value is measured by RVDVI+ viscometer.

Comparative Examples ②~1-15:

An anaerobic adhesive composition was prepared in the same methods

as described in Examples ①~1-13.

Table 2a*. Anaerobic adhesive compositions.

Run		Anaerobic adhesive composition												Thicken- ing agent	
		Basic composition (g)					Hardening promotor								
		M ₁	M ₂	M ₃	M ₄	HQ	QH	A ₁	A ₂	A ₃	CA ₁ (mol)	CA ₂ (mol)	T ₁	T ₂	
①	1	20	10	-	-	003	20	050	010	-	-	0003	-	-	
	2	15	15	-	-	003	20	050	010	-	-	0003	-	-	
	3	10	20	-	-	003	20	050	010	-	-	0003	-	-	
	4	10	20	-	-	004	20	050	010	-	-	0005	-	-	
	5	10	12	6	2	004	20	050	010	-	-	0003	-	-	
	6	10	12	4	4	004	20	050	010	-	-	0003	-	-	
	7	12	12	6	-	004	30	050	010	-	-	0003	-	-	
	8	12	12	-	6	004	30	040	010	-	-	0003	-	-	
	9	12	10	2	6	004	30	040	015	-	-	0003	-	-	
	10	12	10	8	-	004	30	040	015	-	-	0010	-	-	
	11	10	10	10	-	004	30	040	015	-	-	0010	-	-	
	12	10	10	10	-	005	30	040	015	-	-	0010	330	-	
	13	10	10	10	-	005	30	040	015	-	-	0010	450	-	
②	1	20	20	-	-	003	20	050	-	-	-	-	-	-	
	2	15	15	-	-	003	20	050	010	-	-	-	-	-	
	3	15	15	-	-	003	20	050	010	-	-	-	-	-	
	4	10	15	-	-	003	20	050	-	020	-	-	-	-	
	5	10	10	-	-	003	20	030	-	040	-	-	-	-	
	6	10	10	-	-	003	20	030	030	-	-	-	-	-	
	7	10	10	-	-	003	20	050	010	-	0003	-	-	-	
	8	10	10	-	-	004	30	100	010	-	-	0003	-	-	
	9	12	12	-	6	004	30	200	040	-	-	0003	-	-	
	10	12	12	6	-	004	90	050	010	-	-	0003	-	-	
	11	12	12	8	-	001	30	050	010	-	-	0001	-	-	
	12	12	12	8	-	004	30	050	010	-	-	0300	-	-	
	13	12	12	10	-	005	30	045	015	-	-	0010	-	330	
	14	10	10	10	-	005	30	040	015	-	-	0010	-	450	
	15	10	10	10	-	005	30	040	015	-	-	0010	750	-	

* ① : examples; ② : comparative examples; M₁ : ethyleneglycol dimethacrylate; M₂ : 2-hydroxyethyl methacrylate; M₃ : tetraethyleneglycol dimethacrylate; M₄ : urethaneacrylate (Aronics M-1100, Dong-A Synthetic Industrial Co., Japan); HQ : hydroquinone methylether; QH : cumene hydroperoxide; A₁ : *o*-benzoic sulfimide; A₂ : *N,N'*-dimethyl-*p*-toluidine; A₃ : titanium dioxide; CA₁ : oxalic acid; CA₂ : adipic acid; each of CA₁ and CA₂ :

calculated by mol concentration; T₁ : polyethylene powder(5 μ m of average diameter); T₂ : fumed silica(5 μ m of average diameter).

Table 2b*. Physical properties of anaerobic adhesive compositions.

Run		Hardening time (min)	Break-loose torque (kg-cm)	Stability in storage	Viscosity (cp)
①	1	15	61	O	-
	2	13	65	O	-
	3	8	66	O	-
	4	8	69	O	-
	5	9	80	O	105
	6	15	73	O	156
	7	8	86	O	183
	8	9	68	O	232
	9	9	72	O	240
	10	9	86	O	202
	11	8	93	O	214
	12	11	119	O	680
	13	12	129	O	1236
②	1	45	32	O	-
	2	23	34	O	-
	3	370	16	O	-
	4	10	10	X	-
	5	8	55	X	-
	6	22	47	O	-
	7	25	39	O	-
	8	23	45	X	-
	9	150	23	X	232
	10	10	55	X	186
	11	18	37	X	203
	12	10	84	X	211
	13	11	93	X	544
	14	11	101	X	832
	15	39	53	X	-

5 * ① and ② represent examples and comparative ones, respectively.

As shown in Table 2b, anaerobic adhesive compositions using an hardening promoter without difunctional carboxylic acid groups(comparative examples ②~1-7); the anaerobic adhesive compositions using titanium dioxide as an auxiliary oxidizer(comparative examples ②~4,5); the anaerobic adhesive

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composition using oxalic acid (comparative example ②~7); the anaerobic adhesive compositions containing an excessive quantity of reducer and oxidizer as an initiator (comparative examples ②~8,9); the anaerobic adhesive composition using an excessive quantity of urethaneacrylate (comparative example ②~9); the anaerobic adhesive composition containing an excessive quantity of cumene hydroperoxide (comparative example ②~10); the anaerobic adhesive composition using an insufficient quantity of difunctional carboxylic acid (comparative example ②~11) showed relatively longer hardening time and less break-loose torque. By separate samples, the anaerobic adhesive composition using an excessive quantity of difunctional carboxylic acid or fumed silica (comparative examples ②~12-14) showed the increase of acidity in solution, followed by the poor stability in storage. Also, the anaerobic adhesive composition containing an excessive quantity of thickening agent (comparative example ②~15) showed a great difficulty in mixing. On the other hand, comparative examples ②~4, 5, 8-15 showed the poor stability in storage.

Especially, referring to the examples ①~1-13 of this invention, it was found that the break-loose torque of anaerobic adhesive compositions using a thickening agent (examples ①~12,13) was better than that without a thickening agent (examples ①~1-11).

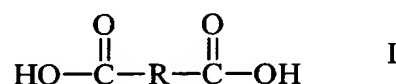
As above-mentioned, the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents in the presence of difunctional carboxylic acid exhibited the rapid velocity in a hardening reaction, the good stability in storage, and the good strength in break-loose torque.

In this context, the anaerobic adhesive composition according to this invention is applicable to the fastening between a bolt and a nut, and the assembly of precision apparatuses and electric/electronic parts.

CLAIMS

What is claimed is:

1. An anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents which blends 0.0001 - 10 parts in weight of a difunctional carboxylic acid, expressed by the following formula I, in proportion to 100 parts in weight of a mixture of monomers and oligomers:



- 10 wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(\text{=CH}_2)$ and n is an integer of 2 to 10.

2. The anaerobic adhesive composition according to claim 1, wherein the difunctional carboxylic acid is one or more selected from malonic acid, succinic acid, adipic acid, itaconic acid, pimelic acid, terephthalic acid and decanoic acid.

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3. The anaerobic adhesive composition according to claim 1, wherein the monomers are one or more selected from ethyleneglycol di(metha)acrylate, diethyleneglycol di(metha)acrylate, triethyleneglycol di(metha)acrylate, tetraethyleneglycol di(metha)acrylate, trimethylolpropane tri(metha)acrylate, styrene, chlorostyrene, vinyltoluene, α -methylstyrene, vinylacetate, methylacrylate, ethylacrylate, butylacrylate and methylmethacrylate.

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4. The anaerobic adhesive composition according to claim 1, wherein the oligomers are one or more selected from mono or poly-(metha)acrylate oligomer of bisphenolic compound containing α, ω -diacryloyl-(bisethyleneglycol)-phthalate and α, ω -tetraacryloyl-(bistrimethylolpropane)-tetrahydrophthalate, and acrylic oligomers having aliphatic/aromatic urethane groups and polyether groups.

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5. The anaerobic adhesive composition according to claim 1, wherein the inhibitors are one or more selected from hydroquinone, methylhydroquinone, hydroquinonemonomethylether, naphthoquinone, penanthraquinone, anthraquinone, sebenzoquinone, catechol, *t*-butylcatechol, 2,6-*t*-butyl-4-methylphenol, phenothiazine, picric acid phenothiazine and hydroxydiphenylamine.

6. The anaerobic adhesive composition according to claim 1, wherein the oxidizers are one or more selected from *t*-butylhydroperoxide, cumenehydroperoxide, di-*t*-butylhydroperoxide, methylethylketoneperoxide, dicumylperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, diisopropylbenzendhydroperoxide, *t*-butylbenzoate and *t*-butylperoxyacetate.

7. The anaerobic adhesive composition according to claim 1, wherein the reducers are one or more selected from phenyl- α -naphthylamine, *N,N'*-dimethyl-*p*-toluidine, *N,N'*-dimethylaniline, triethylenetetramine, diethylenetriamine, tri-*N*-butylamine, *o*-benzoic sulfimide, benzoic acid sulfimide, acetylthiourea, ethylene thiourea and 2-mercaptobenzothiazole.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00285

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C 09 J 4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C 09 J 4/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 06219038 A (IAPC) 19 January 1987 (19.01.87) (abstract) WPI, London, U.K.: Derwent Publications Ltd., Questel/ Orbit, Paris/ France. DW 198708, Accession No. 1987-053881.	1
A	DD 290776 A7 (KOLLOIDCHEMIE GMBH) 13 June 1991 (13.06.91) claims. -----	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 99/00285

Patent document cited in search report			Publicati n date	Patent family member(s)	Publication date
JP	A2	6219038	09-08-1994	none	
DD	A7	290776	13-06-1991	none	